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IMPROVED OXIDATION RESISTANCE OF MOLYBDENUM BY ALLOYING WITH RARE EARTH AND OTHER SELECTED METALS

1 April 1963

Prepared under Navy, Bureau of Weapons
Contract No. NOw 62-0305-d

Interim Report No. 8

1 January 1963 to 28 February 1963

Colorado School of Mines
Research Foundation, Inc.

Golden, Colorado

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COLORADO SCHOOL OF MINES RESEARCH FOUNDATION, INC.

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Report On

IMPROVED OXIDATION RESISTANCE OF
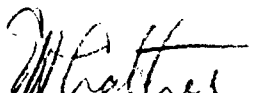MOLYBDENUM BY ALLOYING WITH
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Project No. 311113

TABLE OF CONTENTS

INTRODUCTION

As outlined in Interim Report No. 7 the mathematics has been revamped to calculate values of $C_O D_O$ and D_{Hf}, in order to determine optimum conditions for external scale growth.

SUMMARY

Values of $C_O D_O$ and D_{Hf} have been recalculated on the basis of more accurate equations of the form

$$0.460(Cm \ \tfrac{o}{m} \ K_1)^{2.153} = 2.048(C_O D_O)^{2.153} - K_1^{1.153}(Cm \ \tfrac{o}{m})^{2.153} Dm \quad (1)$$

and

$$K_1^{1.430} \ (Cm \ \tfrac{o}{m})^{2.430} \ Dm = 1.512 \ (C_O D_O)^{2.430} \quad (2)$$

Where $K_1 = \dfrac{X^2}{t}$, $X = cm$, $t = sec$, D_O and $Dm = \dfrac{Cm^2}{sec}$, C_O and Cm = weight percentages of oxygen and metal, and $\dfrac{o}{m}$ = weight ratio of oxygen to metal.

Solutions of these equations give the results shown in Table 1.

TABLE 1

SUMMARY OF VALUES OF C_OD_O AND D_{Hf}

__1300°C__

Experiment No.	Comp. Atom % Hf	C_OD_O	D_{Hf}
5-9a	1.0	$C_{O_1}D_{O_1}=3.893 \times 10^{-10}$	$D_{Hf_1}=23.80 \times 10^{-10}$
5-9b	1.0	$C_{O_2}D_{O_2}=2.576 \times 10^{-10}$	$D_{Hf_1}=23.80 \times 10^{-10}$
5-4a	5.6	$C_{O_3}D_{O_2}=17.25 \times 10^{-10}$	$D_{Hf_2}=26.50 \times 10^{-10}$
5-4b	5.6	$C_{O_4}D_{O_2}=9.20 \times 10^{-10}$	$D_{Hf_2}=26.50 \times 10^{-10}$
5-8a	15.0	$C_{O_5}D_{O_3}=31.30 \times 10^{-10}$	$D_{Hf_3}=47.70 \times 10^{-10}$
5-8aa	15.0	$C_{O_6}D_{O_3}=12.48 \times 10^{-10}$	$D_{Hf_3}=47.70 \times 10^{-10}$

__1200°C__

5-9b	1.0	$C_{O_1}D_{O_1}=3.312 \times 10^{-11}$	$D_{Hf_1}=19.17 \times 10^{-11}$
5-9a	1.0	$C_{O_2}D_{O_2}=1.644 \times 10^{-11}$	$D_{Hf_1}=19.17 \times 10^{-11}$
5-4b	5.6	$C_{O_3}D_{O_2}=15.32 \times 10^{-11}$	$D_{Hf_2}=14.18 \times 10^{-11}$
5-4a	5.6	$C_{O_4}D_{O_2}=5.60 \times 10^{-11}$	$D_{Hf_2}=14.18 \times 10^{-11}$
5-8a	15.0	$C_{O_6}D_{O_3}=4.40 \times 10^{-11}$	$D_{Hf_3}=91.70 \times 10^{-11}$

__1100°C__

5-9b	1.0	----	----
5-9a	1.0	----	----
5-4b	5.6	$C_{O_3}D_{O_2}=5.70 \times 10^{-11}$	$D_{Hf_2}=6.97 \times 10^{-11}$
5-4a	5.6	$C_{O_4}D_{O_2}=3.14 \times 10^{-11}$	$D_{Hf_2}=6.97 \times 10^{-11}$
5-8a	15.0	$C_{O_6}D_{O_3}=8.10 \times 10^{-11}$	$D_{Hf_3}=16.38 \times 10^{-11}$

2. Plots of log C_0D_0 vs $1/T$ and log D_{Hf} vs $1/T$ are shown in Figures 1 and 2.

Figure 3 shows that K_1, which is equal to $\frac{X^2}{t}$ where $X =$ depth of penetration and $t =$ time, increases with temperature under all conditions used in these experiments.

3. External scale formation is favored by high hafnium content, lower temperatures, and lower partial pressures of oxygen. It was previously reported that higher temperatures favored external scale formation. However, the revision of the mathematical equations has shown that this is not the case. Examination of equation (1) shows that the effect of temperature can be shown by determining the variation of $(C_0D_0)^{2.153}/D_m$ with temperature. It increases with increasing temperature. Also, experimental results, Figure 3, support the view that lower temperatures are more favorable. Lowering the temperature below approximately 1200°C, however, results in such a slow rate of oxidation as to be impractical for growing a protective scale. The amount of hafnium that can be used is limited to approximately 17 atom percent, because that is the limit of solid solubility of Hf in Mo. Above this amount of hafnium a new phase is introduced which results in much faster rates of oxidation. A reduced partial pressure of oxygen is the most important variable which can be used to promote external scale formation.
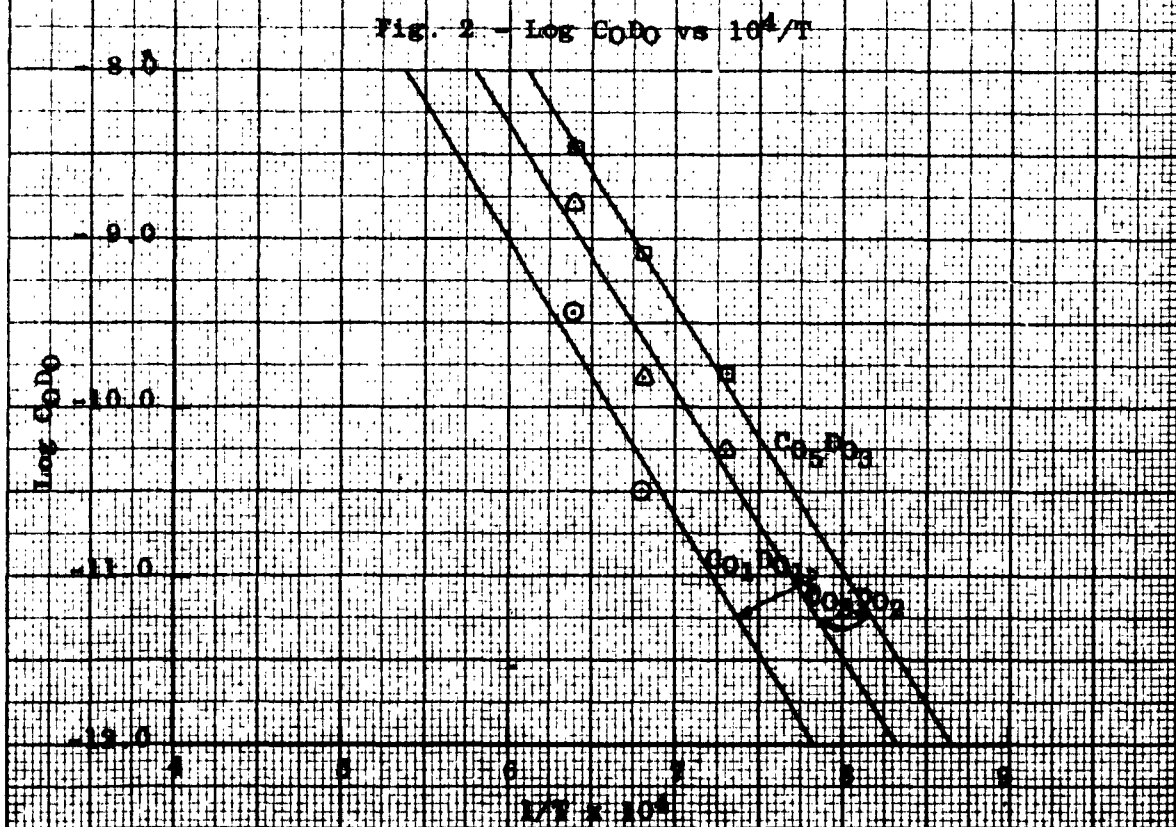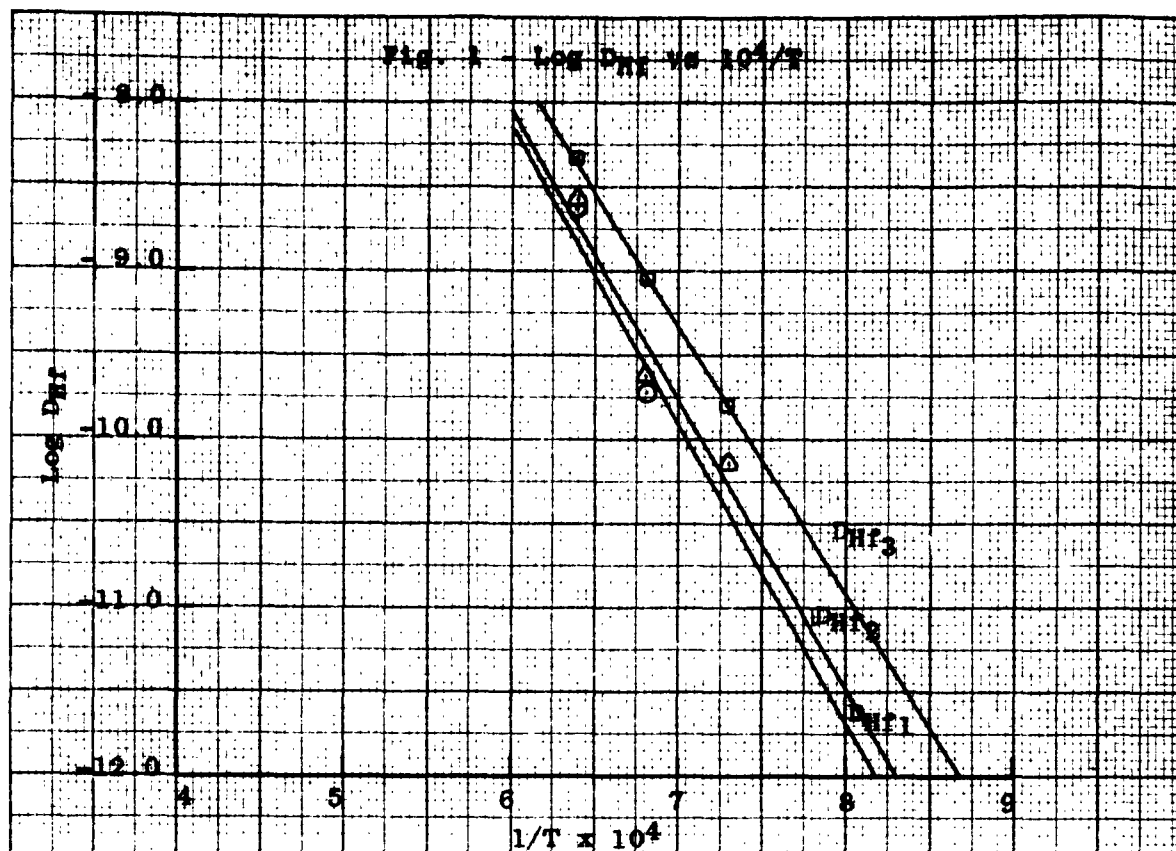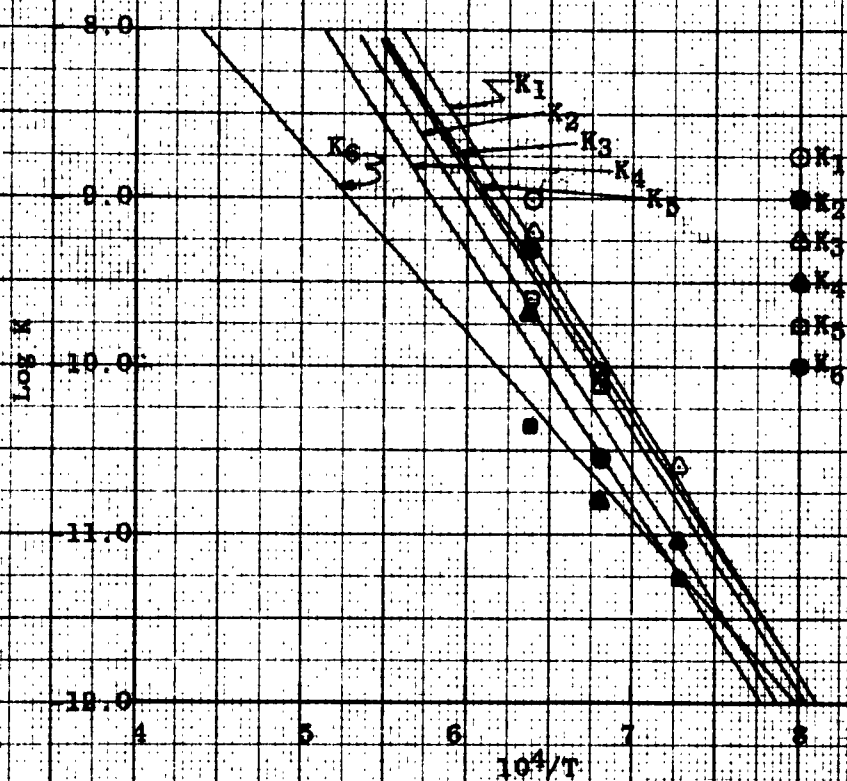
Fig. 1 — Log D_{Hf} vs $10^4/T$

Fig. 2 — Log $C_0 D_0$ vs $10^4/T$

Fig. 8 - Log K vs $10^4/T$

CALCULATIONS

The derivation of equations (1) and (2) will not be shown here, because it is quite lengthy, but it will be completely presented in a future report. Equations of D_0C_0 as a function of Dm were previously reported to be linear (equation 1, Interim Report No. 6), an approximation that was borrowed from the work of Rhines, Johnson, and Anderson[1]. A thorough analysis of the derivation of the diffusion equations they used showed, however, that such an approximation was inadequate in this work, and equations (1) and (2) were developed. Thus, the values of C_0D_0 and D_{Hf} covered by this report supersede those reported in Interim Report No. 6. The calculations are as follow:

TABLE 2

Equations of the form,

$$K_1^{1.153} \left(Cm \frac{o}{m}\right)^{2.153} Dm = 2.048 \, (C_O D_O)^{2.153} - 0.460 \left(Cm \frac{o}{m} K_1\right)^{2.153}$$

Experiment No.	Equation No.	Equation
5-9a	1	$(9.90 \times 10^{-10})1.153(0.3312)2.153 \, D_{Hf_1} = 2.048(C_{O_1} D_{O_1})2.153 - 0.460(0.3312 \times 9.90 \times 10^{-10})2.153$
5-9b	2	$(5.13 \times 10^{-10})1.153(0.3312)2.153 \, D_{Hf_1} = 2.048(C_{O_2} D_{O_1})2.153 - 0.460(0.3312 \times 5.13 \times 10^{-10})2.153$
5-4a	3	$(6.27 \times 10^{-10})1.153(1.79)2.153 \, D_{Hf_2} = 2.048(C_{O_3} D_{O_2})2.153 - 0.460(1.79 \times 6.27 \times 10^{-10})2.153$
5-4b	4	$(2.160 \times 10^{-10})1.153(1.79)2.153 \, D_{Hf_2} = 2.048(C_{O_4} D_{O_2})2.153 - 0.460(1.79 \times 2.160 \times 10^{-10})2.153$
5-8a	5	$(2.556 \times 10^{-10})1.153(4.428)2.153 \, D_{Hf_3} = 2.048(C_{O_5} D_{O_3})2.153 - 0.460(4.428 \times 2.556 \times 10^{-10})2.153$
5-8aa	6	$(0.434 \times 10^{-10})1.153(4.428)2.153 \, D_{Hf_3} = 2.048(C_{O_6} D_{O_3})2.153 - 0.460(4.428 \times 0.434 \times 10^{-10})2.153$

Equations of the form,

$$K_1^{1.430} \left(Cm \frac{o}{m}\right)^{2.430} Dm = 1.512 \, (C_O D_O)^{2.430}$$

Experiment No.	Equation No.	Equation
5-9a	1a	$(9.90 \times 10^{-10})1.430(0.3312)2.430 \, D_{Hf_1} = 1.512(C_{O_1} D_{O_1})2.430$
5-9b	2a	$(5.13 \times 10^{-10})1.430(0.3312)2.430 \, D_{Hf_1} = 1.512(C_{O_2} D_{O_1})2.430$
5-4a	3a	$(6.27 \times 10^{-10})1.430(1.79)2.430 \, D_{Hf_2} = 1.512(C_{O_3} D_{O_2})2.430$
5-4b	4a	$(2.160 \times 10^{-10})1.430(1.79)2.430 \, D_{Hf_2} = 1.512(C_{O_4} D_{O_2})2.430$
5-8a	5a	$(2.556 \times 10^{-10})1.430(4.428)2.430 \, D_{Hf_3} = 1.512(C_{O_5} D_{O_3})2.430$
5-8aa	6a	$(0.434 \times 10^{-10})1.430(4.428)2.430 \, D_{Hf_3} = 1.512(C_{O_6} D_{O_3})2.430$

The ratios $\dfrac{C_{O_2}}{C_{O_1}}$, $\dfrac{C_{O_4}}{C_{O_3}}$, and $\dfrac{C_{O_6}}{C_{O_5}}$ are solved by dividing equation 2a by equation 1a, equation 4a by equation 3a, and equation 6a by equation 5a. When the values are determined they are substituted into equations 1 to 6 so that equations 1 and 2 are in terms of two unknowns, D_{Hf_1} and $C_{O_1}D_{O_1}$, equations 3 and 4 are in terms of two unknowns, D_{Hf_2} and $C_{O_3}D_{O_2}$, and equations 5 and 6 are in terms of two unknowns, D_{Hf_3} and $C_{O_5}D_{O_3}$. The pairs 1, 2; 3, 4; and 5, 6 can then be readily solved for D_{Hf_1}, D_{Hf_2}, D_{Hf_3}, $C_{O_1}D_{O_1}$, $C_{O_3}D_{O_2}$, and $C_{O_5}D_{O_3}$. These results were shown in Table 1.

TABLE 3

1200°C

Equations of the form,

$$K_1^{1.153} \left(Cm \frac{o}{m}\right)^{2.153} \quad Dm = 2.048 (C_0 D_0)^{2.153} - 0.460 \left(Cm \frac{o}{m} K_1\right)^{2.153}$$

Experiment No.	Equation No.	Equation
5-9a	7	$(85.9 \times 10^{-12})^{1.153}(0.3312)^{2.153} D_{Hf1}=2.048(C_{O_1}D_{O_1})^{2.153}-0.460(0.3312 \times 85.9 \times 10^{-12})^{2.153}$
5-9b	8	$(28.03 \times 10^{-12})^{1.153}(0.3312)^{2.153} D_{Hf1}=2.048(C_{O_2}D_{O_1})^{2.153}-0.460(0.3312 \times 28.03 \times 10^{-12})^{2.153}$
5-4a	9	$(78.7 \times 10^{-12})^{1.153}(1.79)^{2.153} D_{Hf2}=2.048(C_{O_3}D_{O_2})^{2.153}-0.460(1.79 \times 78.7 \times 10^{-12})^{2.153}$
5-4b	10	$(15.76 \times 10^{-12})^{1.153}(1.79)^{2.153} D_{Hf2}=2.048(C_{O_4}D_{O_2})^{2.153}-0.460(1.79 \times 15.76 \times 10^{-12})^{2.153}$
5-8a	12	$(28.03 \times 10^{-12})^{1.153}(4.428)^{2.153} D_{Hf3}=2.048(C_{O_6}D_{O_3})^{2.153}-0.460(4.428 \times 28.03 \times 10^{-12})^{2.153}$

Equations of the form,

$$K_1^{1.430} \left(Cm \frac{o}{m}\right)^{2.430} \quad Dm = 1.512 (C_0 D_0)^{2.430}$$

Experiment No.	Equation No.	Equation
5-9b	7a	$(85.9 \times 10^{-12})^{1.430}(0.3312)^{2.430} D_{Hf1}=1.512(C_{O_1}D_{O_1})^{2.430}$
5-9a	8a	$(28.03 \times 10^{-12})^{1.430}(0.3312)^{2.430} D_{Hf1}=1.512(C_{O_2}D_{O_1})^{2.430}$
5-4b	9a	$(78.7 \times 10^{-12})^{1.430}(1.79)^{2.430} D_{Hf2}=1.512(C_{O_3}D_{O_2})^{2.430}$
5-4a	10a	$(15.76 \times 10^{-12})^{1.430}(1.79)^{2.430} D_{Hf2}=1.512(C_{O_4}D_{O_2})^{2.430}$
5-8a	12a	$(28.03 \times 10^{-12})^{1.430}(4.428)^{2.430} D_{Hf3}=1.512(C_{O_6}D_{O_3})^{2.430}$

Again, the ratios $\frac{C_{O2}}{C_{O1}}$, and $\frac{C_{O4}}{C_{O3}}$ are solved by dividing equation 8a by equation 7a, and equation 10a by equation 9a. When these values are determined they are substituted into equations 7 to 10 so that equations 7 and 8 are in terms of two unknowns, D_{Hf_1} and $C_{O1}D_{O1}$, and equations 9 and 10 are in terms of the unknowns D_{Hf_2} and $C_{O3}D_{O2}$. The pairs 7, 8 and 9, 10 can then be readily solved for D_{Hf_1}, D_{Hf_2}, $C_{O1}D_{O1}$, and $C_{O3}D_{O2}$. Equations 12 and 12a can be solved simultaneously for D_{Hf_3} and $C_{O6}D_{O3}$. These results were shown in Table 1.

TABLE 4

1100°C

Equations of the form,

$$K_1^{1.153} \left(Cm \frac{o}{m}\right)^{2.153} Dm = 2.048 (C_0D_0)^{2.153} - 0.460 \left(Cm \frac{o}{m} K_1\right)^{2.153}$$

Experiment No.	Equation No.	Equation
5-9b	13	No oxidation reaction took place
5-9a	14	No oxidation reaction took place
5-4b	15	$(24.75 \times 10^{-12})1.153(1.79)2.153 D_{Hf2}=2.048(C_{O3}D_{O2})^{2.153}-0.460(1.79 \times 24.75 \times 10^{-12})2.153$
5-4a	16	$(9.39 \times 10^{-12})1.153(1.79)2.153 D_{Hf2}=2.048(C_{O4}D_{O2})^{2.153}-0.460(1.79 \times 9.39 \times 10^{-12})2.153$
5-8a	18	$(5.825 \times 10^{-12})1.153 4.428)2.153 D_{Hf3}=2.048(C_{O6}D_{O3})^{2.153}-0.460(4.428 \times 5.285 \times 10^{-12})2.153$

Equations of the form,

$$K_1^{1.430} \left(Cm \frac{o}{m}\right)^{2.430} Dm = 1.512 (C_0D_0)^{2.430}$$

Experiment No.	Equation No.	Equation
5-9b	13a	No oxidation reaction took place
5-9a	14a	No oxidation reaction took place
5-4b	15a	$(24.75 \times 10^{-12})1.430(1.79)2.430 D_{Hf2}=1.512(C_{O3}D_{O2})^{2.430}$
5-4a	16a	$(9.39 \times 10^{-12})1.430(1.79)2.430 D_{Hf2}=1.512(C_{O4}D_{O2})^{2.430}$
5-8a	18a	$(5.285 \times 10^{-12})1.430(4.428)2.430 D_{Hf3}=1.512(C_{O6}D_{O3})^{2.430}$

11

Again, the ratio $\dfrac{C_{O_4}}{C_{O_3}}$ is solved by dividing equation 16a by

equation 15a. When the value is determined it is substituted

into equation 16, so that equations 15 and 16 are in terms of

two unknowns, D_{Hf_2} and $C_{O_3}D_{O_2}$. The equations 15 and 16 can then

be readily solved for D_{Hf_2} and $C_{O_3}D_{O_2}$. Equations 18 and 18a

can be solved simultaneously for D_{Hf_3} and $C_{O_6}D_{O_3}$. These results

were shown in Table 1.

PROPOSED WORK FOR THE PERIOD
MARCH 1, 1963, TO APRIL 30, 1963

1. Now that the role of the three principle independent
variables, temperature, partial pressure of oxygen, and alloy
composition have been more accurately delineated by the mathe-
matics, the future experimental work can be more accurately out-
lined. Maximum outward diffusion of hafnium relative to inward
diffusion of oxygen is promoted by high alloy content, up to a
maximum of approximately 17.0 atom percent hafnium; by lower
temperature, 1200°C being a minimum temperature that allows
any reasonable rate of oxidation; and by lower partial pressures
of oxygen. Therefore the work should now proceed with alloys
of high hafnium content at 1200°C to 1300°C and with reduced
partial pressures of oxygen. The partial pressures of oxygen
obtained previously, after passing the hydrogen through a dry
ice trap, were much higher than they ought to have been because
of the oxygen partial pressure of the refractory mullite furnace
tube. Molybdenum tubes, of slightly smaller diameter than the
mullite tubes, and extending approximately two inches on either
side of the hot zone of the furnace, were inserted in the furnace
in all of this work. It was thought that this would prevent
any partial pressure of oxygen from the mullite tube from
entering the oxidation reaction zone. Apparently, some back
diffusion of oxygen did take place. The work will now be done
with more stable refractory oxide tubes. Zirconia will be the
first one to be tried.